HIGH VANADIUM CONCENTRATIONS IN GROUNDWATER AT EL HIERRO (CANARY ISLANDS, SPAIN)

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Abstract

High concentrations of Vanadium have been measured in the groundwaters of the volcanic island of El Hierro. Values ranging from 19.4 to 288 μg/L are much higher than those generally found in natural water samples (< 1 μg/L). Such increased contents mainly derive from the water-rock interaction processes within the aquifer formed by Vanadium-rich basaltic rocks. The mobility of Vanadium in these groundwaters is further enhanced by their oxidizing and alkaline conditions. Possible consequences on human health due to the consumption of these V-rich waters should be investigated.

1. Introduction

Drinking water quality has a heavy impact on human health. Despite being more protected to microbiologic contamination than surface water, due to prolonged water-rock interaction, groundwater could reach unsafely high levels of inorganic contaminants. Among these, trace elements have long been disregarded although some of them (As, Cd, Hg, Pb) are highly toxic.

Vanadium is a potentially toxic trace element widely distributed in the earth's crust at an average concentration of about 120 mg/Kg (Reimann and de Caritat 1998). Because of its affinity for oxygen, V forms both stable oxyanions and oxycations. V is a redox sensitive element that exists in three oxidation states in the environment: +3, +4, and +5. Pentavalent Vanadium is chemically more stable, and it represents the most toxic form (WHO 1988). In most common environmental conditions it is found as $H_2VO_4^-$ or HVO_4^{2-} oxyanion. Tetravalent Vanadium can be found as $V(OH)_3^+$ or in very acidic conditions as VO^{2+}, while trivalent Vanadium is found only in reducing conditions as $V(OH)_2^+$ in low concentrations due to its very low solubility (Wright and Belitz 2010). The mobility of the most soluble penta- and tetravalent forms in groundwater is in part controlled by the adsorption/desorption processes and the formed ionic compounds are often strongly adsorbed to mineral surfaces via inner-sphere complexation. Similarly to As, V contents can be strongly controlled by precipitation of solid phases such as Fe-oxyhydroxides (Aiuppa *et al.* 2000).

Vanadium is biologically active and is an essential nutrient for many animals with a suggested role in peroxidase enzymes, although its precise biochemical function is still in some doubt (WHO 1996). An intake of over 10 mg V per day can be toxic for adults, but this greatly depends on its speciation and oxidation state (WHO 1996). In severe cases, toxic levels of V causes the inhibition of certain enzymes, which has several neurological effects, and can cause breathing disorders, paralyses and negative effects on the liver and kidneys.

Vanadium compounds have insulin-mimetic properties. First reports on therapeutic properties of Vanadium compounds in diabetes appeared as early as in 1899 (Thompson and Orvig 2006). Many studies were conducted on inorganic and organic Vanadium derivatives in induced-diabetes animal models, in which the studied compounds were found to impact the levels of glucose, cholesterol and triacylglycerols, with no harmful side effects upon prolonged administration (Korbeki *et al*. 2012).

The main natural sources of Vanadium are water-rock interaction processes while anthropogenic sources of this metal are mainly oil and coal combustion, steel alloy tool production and traffic pollution (WHO 1988).

Concerns over the possible adverse health effects to humans from high concentrations of V in drinking water have led the U.S. Environmental Protection Agency to place V on its most recent contaminate candidate list (U.S. E.P.A. 2012). These same concerns also led the California Department Public of Health (CDPH) to establish a notification level (NL) of 50 μg/L for V in drinking water (CDPH 2007). For the same reasons in Italy, the Superior Council of Health in 1995 indicated as a limit value of Vanadium in drinking water the concentration of 50 μg/L (SCH 2001).

Drinking water sources of good quality are generally limited on islands and El Hierro makes no exception. The purpose of this paper is to provide preliminary information about the groundwater quality of the island focusing on their Vanadium contents.

2. El Hierro island

2.1 Geological setting

El Hierro is the smallest and westernmost of the Canary Islands. Its surface is 270 Km^2 and its highest peak rises 1501 m asl (Malpaso). Three main volcanic units (Figure 1) can be distinguished (Carracedo *et al*. 2001): Tiñor volcano (the first subaerial edifice), El Golfo edifice and the rift volcanism. Three rifts NW, NE and S oriented respectively, forming angles of 120º, morphologically divide this triangular shaped island. Quaternary basaltic and trachybasaltic lava flows formed the emerged part of the island where hundreds of young cinder cones and lava flows are located. The oldest subaerial rocks in the island are dated at 1.12 Ma (Guillou *et al*. 1996). Three main gravitational collapses are evidenced: Las Playas, El Julan and El Golfo.

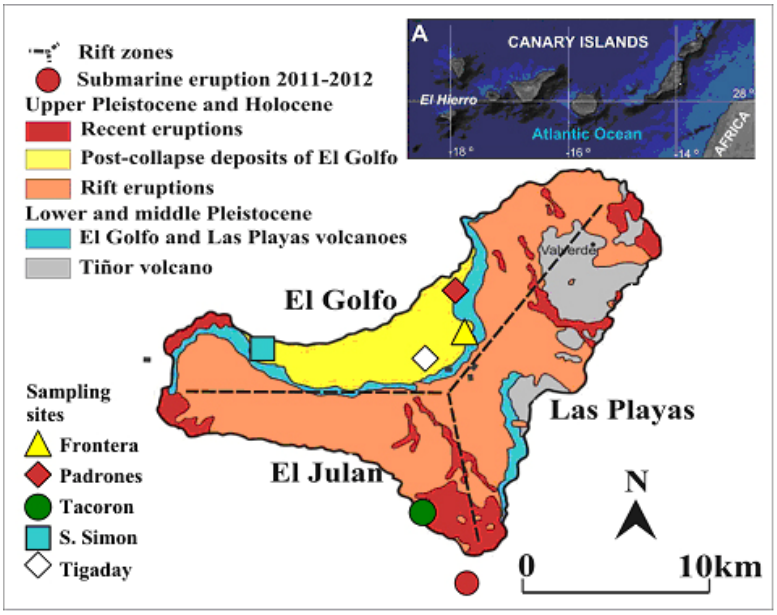

Figure 1. Geology of El Hierro (after Martí et al 2013) and location of the sampling sites.

El Hierro lavas range from basanites and picrobasalts to trachytes (Stroncik *et al*. 2009). Tiñor and El Golfo lavas range from picrobasaltic to hawaiitic-tephritic compositions. At El Golfo also trachytic lavas can be found. Picrobasalts, basanites and tephrites are main products from the rifts (Carracedo *et al*. 2001; 2002).

2.2 Recent volcanic activity

Despite being the youngest of the Canary Islands, only questionable records of one historical eruption have been found at El Hierro, Lomo Negro AD1793(?) (Hernández-Pacheco 1982).

On 10th October 2011, a submarine volcanic eruption started 2 Km south El Hierro Island. By the time the eruption started, almost 10000 earthquakes had been located and the deformation analyses showed a maximum deformation of more than 5 cm (López *et al*. 2012). After the end of the submarine eruption on March 2012 and up to now, several volcanic unrest processes have taken place in the island. The most relevant ones started on June 2012 and March 2013. Each of these periods has been evidenced by intense seismicity and ground deformation.

2.3 Hydrogeological outline

Water resources in the island are limited to groundwater due to the irregularity of the precipitation and the characteristics of the terrain that favors infiltration instead of surface runoff, resulting in the lack of permanent surface water resources. The number of springs is limited and their discharge is low, estimated in about 250 m^3/year (Plan Hidrológico Insular de El Hierro 2002).

The hydrogeology of the island is mainly governed by the structural rifts and the associated phenomena (dykes and fractures) and these elements modify the hydrogeologic properties of the different geologic units (Lamoneda González 1990). A particular situation is observed in El Golfo area with the superposition of two aquifers (Lamoneda González, 1990). Groundwater circulation is mostly radial in the direction of the rifts, with vertical flux in the unsaturated zone and horizontal, in the same radial direction, in the saturated zone (Lamoneda González 1990).

The phreatic surface is located at different quotes inside the island. At the coastline it is coincident with the sea level, where discharge takes place. Moving through the centre of the island, the level of the water table ascends softly. The precise level in the central part of the island is unknown because of the absence of wells reaching the phreatic surface in that area (Navarro Latorre *et al*. 1994).

Regarding the quality of groundwater, the main problems in the island are presence of CO_2 and marine intrusion (Navarro Latorre *et al*. 1994).

Precipitation in the island is characterized by extreme irregularity and intensity. Near the coast values range between 100-300 mm/year and it increases significantly with the altitude. The maximum values range 600 mm/year in the central and north areas. In the southwest, precipitation has medium values of 400 mm/year. There is also horizontal precipitation in the island originated by orographic clouds. The estimated volume of groundwater abstracted is 1.9 hm^3/year (Plan Hidrológico Insular de El Hierro 2002).

3. Materials and Methods

Water samples were collected repeatedly at five groundwater sampling sites: San Simón, Frontera, Tigaday, Tacorón and Los Padrones (Figure 1). San Simón is a non productive well-gallery 25 m deep and with two radial galleries 18 and 15 m long respectively. Los Padrones is a well-gallery 51.5 m deep and 270 m long used for agriculture and population supplying and has a yield of about 3300 m^3/d. Frontera is a canarian well 235 m deep used for agriculture and has a yield of about 1800 m^3/d. Tigaday is a well-gallery 282 m deep with two radial galleries 164 and 113 m long used for agriculture and population supplying and has a yield of about 550 m^3/d. Tacorón is a gallery 1510 m long used for irrigation and limited drinking water supply.

About 200 samples were collected in the period from July 2011 to December 2013. The main physico-chemical parameters were measured in the field with portable instruments. Major ions were determined at the IGME (Instituto Geológico y Minero de España) water laboratory with atomic emission spectroscopy (K and Na), spectrophotometer atomic absorption (Ca and Mg), titration (alkalinity) and ionic chromatography (Cl and SO_4), while V and other trace element contents were determined with ICP-MS.

4. Results

4.1 Water chemistry

The sampled groundwaters are mostly cold (< 22 °C) low salinity waters (El. cond. 300-1200 µS/cm) with slightly alkaline pH (7-8.5). Only the waters collected at San Simon well, which can be considered as slightly thermalised, show higher temperatures (~25 °C) and salinities (El. cond. ~4000 µS/cm). Major ion concentrations (Figure 2) indicate a water composition ranging from Alkaline-Bicarbonate (San Simón, Tigaday and Los Padrones) to Alkaline-Chloride (Frontera and Tacorón). The positive relationship between Alkalinity and major cations indicate that dissolved ions mainly derive from incongruent dissolution of the silicate minerals of the volcanic rocks of the island driven by elevated dissolved CO_2. Like in other active volcanic systems, the latter is mainly originated from magmatic activity (Aiuppa *et al.* 2000; 2003). A significant seawater contribution can be recognized at least in the Alkaline-Chloride waters. Such contribution mainly derives from the sea-spray component of the meteoric recharge although limited seawater intrusion has been evidenced.

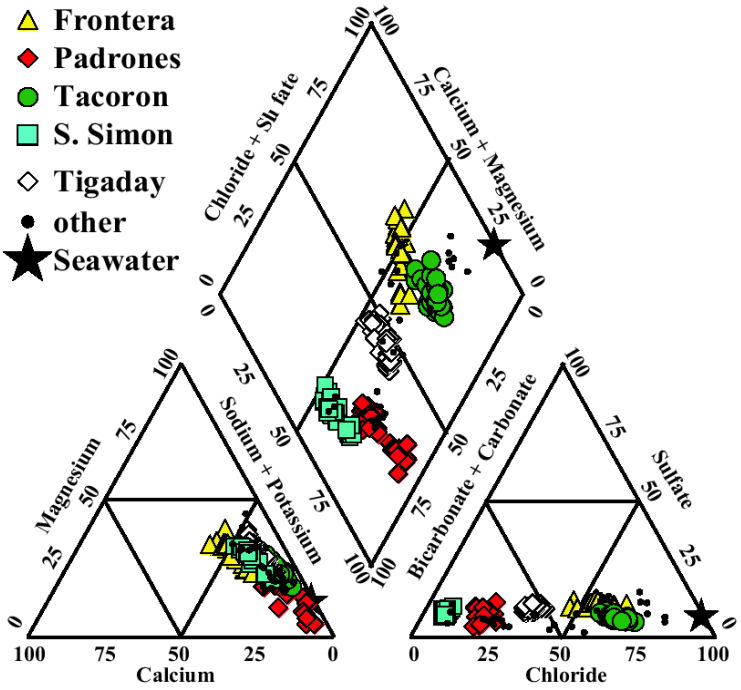

Figure 2. Piper diagram showing the water composition of the sampling sites.

4.2 Vanadium contents

Of the collected water samples 173 have been analyzed also for Vanadium and the obtained concentrations range from 19.4 to 288 µg/L. The median concentrations for the five sampling sites are 37.3 for San Simon, 70.8 for Frontera, 91.6 for Tigaday, 108 for Los Padrones and 210 for Tacoron (Table 1). Vanadium concentrations do not show any strong positive or inverse relationships with the major ions. A possible inverse relationship could be found with the Iron content probably due to surface adsorption on amorphous Fe-oxyhydroxides that form in the shallow oxidizing environment. Positive relationships with As, Mo and Se, due to their similar geochemical behavior, can also be recognized.

Table 1. pH, Electric Conductivity (µS/cm @ 20°C) and major ion concentrations (mg/L) in the groundwater of El Hierro. Alkalinity expressed as mg/L of HCO_3.

		pH	EC	Na	K	Mg	Ca	Cl	NO_3	SO_4	Alk.
Frontera	Min	6.89	553	78	14	22	17	104	5	38	107
	Max	8.13	959	103	25	47	48	220	13	66	167
	Median	7.62	823	93	18	37	28	174	8	56	149
Padrones	Min	6.96	326	45	8	3	1	19	11	8	129
	Max	8.19	382	76	12	11	9	31	16	25	154
	Median	7.72	333	51	11	9	3	24	14	16	140
Tacoron	Min	7.10	1002	132	23	33	7	236	3	47	189
	Max	8.34	1388	232	37	59	18	368	7	67	240
	Median	7.86	1172	199	29	42	13	280	5	57	206
Tigaday	Min	7.36	510	81	11	24	6	18	3	36	299
	Max	9.24	977	200	19	51	33	37	14	78	610
	Median	7.68	928	136	16	46	25	31	7	62	576
S. Simon	Min	7.19	3680	477	36	154	53	470	9	231	1210
	Max	8.01	4400	835	58	220	78	684	29	320	1660
	Median	7.66	3930	684	46	172	65	572	21	266	1520

Table 2. Vanadium concentrations (µg/L) in the groundwater of El Hierro

Sampling site	S. Simon	Frontera	Tigaday	Padrones	Tacoron
minimum	32.4	44.1	19.4	46.2	125
1st quartile	35.9	67.9	83.8	105	199
median	37.3	70.8	91.6	108	210
average	40.0	72.9	89.2	111	219
3rd quartile	39.5	74.9	97.6	114	235
maximum	120	105	114	218	288
n. of samples	34	32	39	41	27

5. Discussion

5.1 Origin of Vanadium in El Hierro groundwaters

Although not abundant, literature data on Vanadium concentrations in natural waters show that this element has generally values below 1 µg/L (Table 2). Only groundwaters circulating in mafic volcanic rocks (Mt. Etna, Italy) and/or ultramafic rocks (California) show values exceeding tens of µg/L reaching values of some hundreds of µg/L (Table 2). The high levels in these waters are the direct consequence of the higher release of this metal from V-rich rocks of the aquifers. Basaltic rocks show, in fact, the highest Vanadium concentrations among the most diffused crustal rock types (Table 3 – Reimann and de Caritat 1998).

The island of El Hierro is almost completely composed of basaltic rocks with only limited outcrops of more evolved volcanic rocks (Carracedo *et al*. 2001). The Vanadium content of the basaltic rocks of the island, from the oldest to the most recent, show elevated values (201-365 mg/Kg – Table 4) (Carracedo *et al*. 2001). Only the quantitatively negligible evolved volcanic rocks show lower concentrations (34.6 mg/Kg – Table 4).

Water-rock interaction processes acting on meteoric derived waters, enhanced by magmatic derived CO_2 dissolution, drive groundwaters' composition at El Hierro. Solutes in the analyzed groundwaters originate mainly from the incongruent dissolution of the silicate minerals of the aquifers' rocks. The high to very high Vanadium concentrations measured in the groundwaters

from El Hierro can be therefore easily justified by the V-rich composition of basalts that form the aquifers on the island. The small seawater component, sometimes recognized in these groundwaters, cannot contribute significantly to the Vanadium burden being ocean water not particularly enriched in this element (1-3 μg/L). Anthropogenic sources of Vanadium are also absent on the island.

Finally, the peculiar Vanadium concentrations of the groundwaters are also favored by their chemical-physical conditions. As previously highlighted by Wright and Belitz (2010), Vanadium is highly mobile in oxidized and alkaline conditions like those prevailing in the sampled waters. The sampled groundwaters all display a mildly alkaline (pH median values between 7.6 and 7.9) and mildly oxidizing (Eh between 100 and 200 mV) values.

Table 3. Vanadium concentrations (μg/L) in natural waters

	Etna GW	EU tap	EU bottle	Norw GW	EU streams	Calif GW	Arg GW
reference	(1)	(2)	(2)	(3)	(4)	(5)	(6)
min	0.80	0.05	0.05	0.01	0.01	< 3	0.05
1st quartile	7.56	0.05	0.05	0.09	0.23	n.r.	0.36
median	18.7	0.17	0.17	0.24	0.46	5	0.51
average	27.6	0.53	0.65	0.52	0.83	n.r.	0.55
3rd quartile	39.1	0.43	0.41	0.57	0.87	n.r.	0.67
max	384	13.7	48.9	13.9	19.5	140	2.47
n. of samples	234	579	884	476	808	8470	101

References: (1) groundwaters of Mt. Etna (Italy) - Aiuppa et al. 2003; (2) European tap waters and bottled waters – Reimann and Birke 2010; (3) Norwegian bedrock groundwaters – Frengstad et al. 2000; (4) European stream waters – De Vivo et al. 2006; (5) California groundwaters – Wright and Belitz 2010; (6) Argentina Pampean groundwaters – Fiorentino et al. 2007: n.r. = not reported

Table 4. World Average Vanadium concentrations in rocks (Reimann and de Caritat 1998)

	V mg/Kg
Bulk continental crust	120
Upper continental crust	60
ultramafic rock	80
ocean ridge basalt	250
gabbro, basalt	260
granite, granodiorite	70
Sandstone	20
Greywacke	98
Shale, schist	130
Limestone	15
Coal	40

5.2 Human health considerations

Due to the generally low concentrations, water intake is not considered among the major sources of Vanadium to the human body (WHO 1988). Until now, no maximum admissible concentration or guideline value for drinking water has been therefore issued by the World Health Organization (WHO 1996). Only a few national legislations set a limit for Vanadium with very different values varying from 1 μg/L in Serbia to 100 μg/L in Czech Republic and Ukraine (Reimann and Birke 2010).

Table 5. Vanadium and silica concentrations in rocks of El Hierro

Age of the sample	Reference	SiO_2 %	V mg/Kg
2011 A.D.	Martí *et al*. 2013	42.84	342
1790 A.D. (?)	Carracedo *et al*. 2001	41.33	365
15 ka	Carracedo *et al*. 2001	44.64	277
44 ka	Carracedo *et al*. 2001	44.16	282
76 ka	Carracedo *et al*. 2001	41.19	365
158 ka	Carracedo *et al*. 2001	45.30	248
176 ka	Carracedo *et al*. 2001	55.61	34.6
261 ka	Carracedo *et al*. 2001	44.30	230
442 ka	Carracedo *et al*. 2001	47.27	201
545 ka	Carracedo *et al*. 2001	41.45	316
1.04 Ma	Carracedo *et al*. 2001	45.67	263
1.05 Ma	Carracedo *et al*. 2001	44.46	263
1.11 Ma	Carracedo *et al*. 2001	46.17	248
1.12 Ma	Carracedo *et al*. 2001	43.41	327

In Italy, the Superior Council of Health in 1995 indicated a provisory limit of 50 μg/L (SCH 2001). This created a "Vanadium case" due to the fact that most of the waters of the volcanic aquifers in central Italy and in eastern Sicily did not comply with the new limit (Aiuppa *et al*. 2003). In view of the inability to respect the 50 μg/L limit by water distribution systems serving large population groups, especially in the Etnean area in Sicily, and of the lack of evidence of overt toxicity, the limit value was provisionally raised by the Superior Council to 120 μg/L in 2000 and to 140 μg/L in 2011 (Crebelli and Leopardi 2012).

Due to the fact that drinking water supply on El Hierro relies exclusively on groundwater, the application of a 50 μg/L limit would deprive completely the inhabitants of the island of their drinking water resources. Also the less stringent values (100-140 μg/L) would limit the available resources. Since alternative V-poor resources are either difficult to find or to expensive, some V-removal technique should be applied to the groundwater before its distribution as drinking water.

Finally since Vanadium toxicity and the effects of V-rich consumption of human health should be investigated in depth, El Hierro could be considered an interesting natural laboratory.

6. Conclusions

The groundwaters of the basaltic aquifers of El Hierro island revealed very high Vanadium concentrations. Measured values (19.4 to 288 μg/L) are up to three orders of magnitude higher than average worldwide groundwater concentrations. These high concentrations originate from the incongruent dissolution of the silicate minerals that constitute the aquifer rocks of the island driven by the dissolution of magmatic CO_2. Basaltic rocks, which are the most Vanadium enriched rocks of earth's crust, constitute almost exclusively the bulk of the island. Furthermore, the slightly alkaline and oxidizing conditions of the El Hierro groundwaters favor the formation of soluble ionic Vanadium compounds.

At present no maximum admissible concentration or guideline value has been defined by the World Health Organization but the highest values found on the island have to be considered as potentially unhealthy for long term human consumption.

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